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(21) International Application Number: PCT/GB99/00737 (22) International Filing Date: 22 March 1999 (22.03.99) (30) Priority Data: 9805880.3 20 March 1998 (20.03.98) GB (71) Applicant (for all designated States except CA FR US): SOF-ITECH N.V. [BE/BE]; 140, rue de Stalle, B-1180 Brussels (BE). (71) Applicant (for FR only): COMPAGNIE DES SERVICES DOWELL SCHLUMBERGER S.A. [FR/FR]; 50, avenue Jean Jaures, F-92541 Montrouge (FR). (71) Applicant (for CA only): SCHLUMBERGER CANADA LIMITED [CA/CA]; 24th floor, Monenco Place, 801 6th Avenue, S.W., Calgary, Alberta T2P 3W2 (CA). (72) Inventors; and (75) Inventors/Applicants (for US only): JONES, Timothy, Gareth, John [GB/GB]; 242 High Street, Cottenham, Cambridge CB4 8RZ (GB). TUSTIN, Gary, John [GB/GB]; 8 Carrick Close, Cambridge CB1 8RQ (GB).		(74) Agent: MIRZA, Akram, Karim; Schlumberger Cambridge Research Limited, High Cross, Madingley Road, Cambridge CB3 0EL (GB). (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: HYDROPHOBICALLY MODIFIED POLYMERS FOR WATER CONTROL		
(57) Abstract		
<p>The use of a hydrophobically modified water soluble polymer is described capable of being chemically cross-linked so as to produce a stable gel for blocking a water-bearing formation from a hydrocarbon-producing well. The polymer is essentially linear having hydrophilic side groups located at random positions along its backbone.</p>		

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Hydrophobically Modified Polymers for Water Control

The present invention relates to cross-linkable hydrophobically modified water-soluble polymers for reducing the water
5 production of a hydrocarbon well drilled through subterranean formations. More particularly it relates to such polymers and polymer containing compositions for selectively reducing the flow of subterranean aqueous fluids into a well while maintaining the hydrocarbon production.

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BACKGROUND OF THE INVENTION

During the life cycle of a hydrocarbon well, e.g., a well for
15 extracting oil or natural gas from the Earth, the producing well commonly also yields water. In these instances, the amount of water produced from the well tends to increase over time with a concomitant reduction of hydrocarbon production. Frequently, the production of water becomes so profuse that remedial measures
20 have to be taken to decrease the water/hydrocarbon production ratio. As a final consequence of the increasing water production, the well has to be abandoned.

Various techniques have been developed and used for reducing the
25 quantity of water produced from oil and/or gas wells. For example, US Pat. No. 3,719,228 discloses a method of treating a subterranean formation containing hydrocarbons and brine to stimulate the production of hydrocarbons: A preflush composition comprised of a water solution of rosin soap and fatty acid soap
30 is injected into the formation. The preflush reacts with connate brine to produce a precipitate that blocks the brine-bearing passages. The composition does not react with hydrocarbons thereby allowing hydrocarbon-bearing passages to remain open. Another alternative method is disclosed in US Pat. No.
35 4,617,132: A sandstone formation is contacted with an aqueous solution containing a water soluble anionic polymer having a molecular weight greater than 100,000. As the next step, the

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anionic polymer is contacted with a fluid containing a water soluble cationic polymer having a weight greater than 1,000. As a result of the contact of the anionic with the cationic polymer, coacervation occurs between the two polymers which reduces the amount of the anionic polymer removed from the formation by fluids produced therefrom. The presence of stabilized polymer in the formation reduces the water/oil ratio by reducing the permeability of the formation to water in the wellbore area.

In yet another technique, disclosed in US Pat. No. 5,203,834, comprises the steps of injecting a gas, a polymer composition capable to form a foamed gel with the gas, and a delayed gel degrading agent being capable of opening pathways in the gel.

The gelation of high molecular weight polymers ($M_w > 10^6$ g/mol) has been extensively used in the development of water-based treatment fluids for water control is further described for example by R. D. Sydansk in "Acrylamide-polymer/chromium(III)-carboxylate gels for near wellbore matrix treatments", 7th SPE Symp. Enhanced Oil Recovery, Tulsa, Ok., April 1988, SPE/DOE 20214, or by R. S. Seright in: "Placement of gels to modify injection profiles", SPE/DOE Symp. Enhanced Oil Recovery, Tulsa, Ok., April 1994, SPE 27740. Typically for those methods, an aqueous solution of a high molecular weight polymer, such as a polyacrylamide/polyacrylate copolymer (a so-called partially-hydrolysed polyacrylamide), is gelled in situ in a porous formation using a metal cross-linker such as Cr^{3+} or small water-soluble organic cross-linkers such as formaldehyde and formaldehyde/phenol. Other water-soluble polymers such as poly(vinyl alcohol), the polysaccharide guar gum and the copolymer poly(vinylpyrrolidone-co-2-acrylamido-2-methyl-1-propanesulphonic acid) which can be cross-linked with a variety of cross-linking agents such as Zr^{4+} and boric acid.

A more recent approach is described by A. Keller and K. A. Narh in: "The effect of counterions on the chain conformation of polyelectrolytes, as assessed by extensibility in elongational

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flow: the influence of multiple valency", J. Polym. Sci.: Part B: Polymer Phys., 32, 1697-1706 (1994). It includes the cross-linking of poly(sodium 4-styrenesulphonate) using Al^{3+} ions to form a gel. The concentration of the high molecular weight hydrophilic polymers used to form hydrogels is typically in the range 3-10 g/l.

Hydrophobically-modified polymers as such and their application as thickening agents in aqueous fluids has been extensively described. The principal application of these polymers is as viscosifying agents and they are commonly referred to as associative thickeners; these polymers are also known as polysoaps. The associative behaviour is generated by a small mole fraction (typically ≤ 0.05) of hydrophobic groups which, as separate monomers, are not soluble in water. The hydrophobic groups undergo intermolecular association in aqueous solution above the overlap concentration which results in a significant increase in solution viscosity.

Hydrophobically-modified polymers can be gelled in the presence of monomeric surfactants. For example, large increases in the viscosity of solutions of hydrophobically-modified poly(acrylic acid) in the presence of anionic, cationic and non-ionic surfactants have been disclosed. A brief review of the interaction between hydrophobically-modified polymers and surfactants can be found in: Lindman, B. and Thalberg, K., "Polymer-surfactant interactions - recent developments" in Interactions of Surfactants with Polymers and Proteins, E.D. Goddard and K.P. Ananthapadmanabhan (eds.), pp. 203-276, CRC Press, Boca Raton, Florida (1992).

In the U.S. Patent No. 4,532,052, the use of branched organic polymers for various well treating operations is described. The known polymers include hydrophilic and combinations of hydrophilic and hydrophobic side groups. The preferred examples are characterized as having large hydrophilic branches.

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In the U.S. Patent No. 5,003,006, there are described cross-linked block copolymers containing polar and non-polar segments, with the polar segments generally making up at least 50 per cent.

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It is the object of the invention to provide new polymers for water control application.

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SUMMARY OF THE INVENTION

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According to a first aspect of the invention, hydrophobically modified water-soluble polymers are provided which are capable of being chemically cross-linked to produce permanent gels in water-bearing formations. The polymers are characterized by a linear chain or backbone and attached thereto hydrophobic side groups at random locations. The term "linear" is defined as the absence of extended side groups/chains others than the hydrophobic groups. The term "extended" can be interpreted as having a molecular weight of more than 200.

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It has been found that hydrophobically modified polymers when based on block copolymers, tend to form an inferior gel presumably due to presence of inhomogeneous gelation. In addition there is economic advantage when producing polymers with high molecular weight through a random co-polymerization process. The use of large polymers is advantageous as it reduces the polymer concentration required to achieve a desired level of viscosity. Within the scope of the present invention, a high molecular weight can be defined as a molecular weight in excess of 50,000, more preferably in excess of 100,000. A preferable upper limit for the size of the polymers is given by a molecular weight of 15 million, preferably 5 million, more preferably 500,000 or less.

The polymers preferably comprise low concentrations (0.5-5 mole percent) of hydrophobic monomers which randomly co-polymerise with the hydrophilic monomers to form random copolymers. The

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- hydrophilic units of the polymer, which constitute preferably 95-99.5 mole percent of the polymer chain, contain preferably at least some small fraction of functional groups which can be chemically cross-linked to produce a gel. Alternatively, the
- 5 hydrophobic groups themselves can contain chemical functions which can be the sites of cross-linking. Preferred hydrophobic groups are alkyl groups of more than six , preferably eight, and even more preferably 12 carbon atoms, and derivatives thereof.
- 10 Chemical cross-linking is defined as forming a chemical bond between the cross-linked polymers. Chemical cross-linking is understood to be stable and thermally irreversible. Some of the advantages in the use of hydrophobically modified polymers are responsiveness to hydrocarbons resulting in a reduction in the
- 15 adhesive strength of gels and an extreme retardation of gelation, and solubilisation of large organic cross-linking agents.

- The cross-linking agents can be either inorganic ions (or ionic
- 20 complexes) or polar organic molecules. When the polymer contains ionic groups such as carboxylate or sulphonate functions the polymer chains can be cross-linked by inorganic ions such as chromium(III) or zirconium(IV), frequently in the presence of ligands, such as acetate or adipate ions, to control the rate of
- 25 cross-linking. Alternatively, organic cross-linking agents can be used. For example, the amide groups on poly(acrylamide) can be cross-linked with formaldehyde or a mixture of formaldehyde and phenol. The disadvantages of using formaldehyde or similar small molecules are their toxicity and issues of disposal. The
- 30 larger reagents such as hexanal and heptanal, which are not classed as toxic, would be suitable cross-linking agents but are not sufficiently soluble in water to cross-link normal hydrophilic polymers such as the poly(acrylamide)/poly(acrylate) copolymer. However, these larger cross-linking agents are
- 35 solubilised in aqueous solutions by hydrophobically-modified poly(acrylamide) polymers and can thence cross-link them.

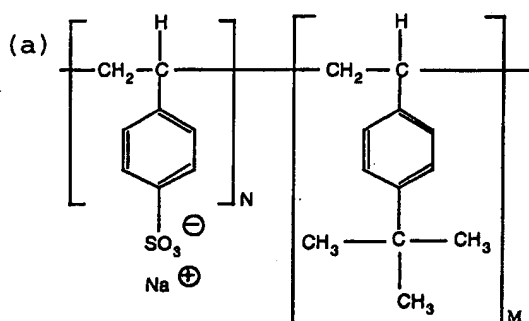
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These and other features of the invention, preferred embodiments and variants thereof, and further advantages of the invention will become appreciated and understood by those skilled in the art from the detailed description following below.

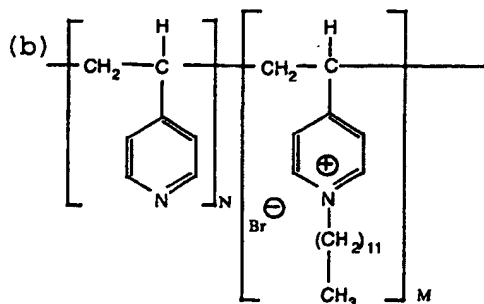
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MODE(S) FOR CARRYING OUT THE INVENTION

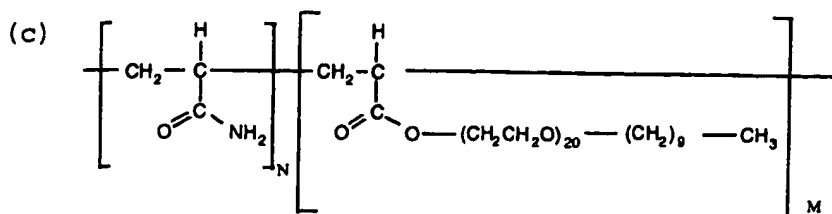
A large number of hydrophobically-modified polymers are known as
 10 such and suitable for the purpose of the present invention. These polymers are based on the modification of common water-soluble (hydrophilic) polymers such as poly(acrylamide), poly(acrylic acid), poly(vinylpyridine), hydroxyethylcellulose and poly(ethylene oxide). The structure of examples of
 15 hydrophobically-modified polymers are given below for poly(sodium 4-styrenesulphonate) (a), poly(vinylpyridine) (b), and poly(acrylamide) (c) :



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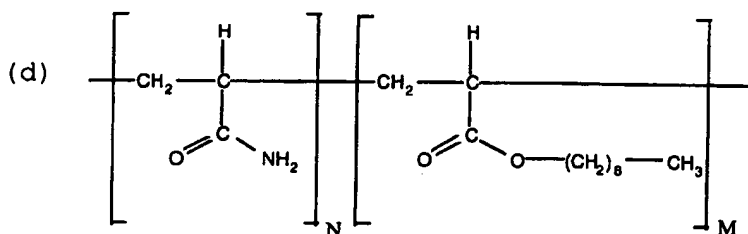


The fraction $M/(M+N)$ denotes the mole fraction of hydrophobic monomers in the polymer.

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The following formulae describe the structure of further examples which can be readily cross-linked using known cross-linkers.

- 10 The structure of a hydrophobically-modified poly(acrylamide) where the hydrophobic modification takes the form of replacing about 3 mole percent ($M/(M+N)=0.03$) of the acrylamide units with the hydrophobic monomer n-nonyl acrylate is:



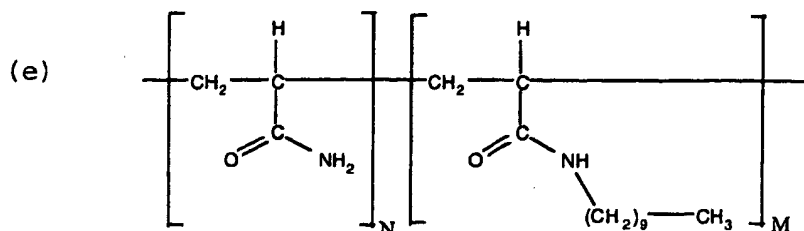
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- This polymer has an average molecular weight of about 5×10^6 g/mole and it can be readily cross-linked with chromium(III) or zirconium(IV) or the organic cross-linker hexanal. Where the gels formed by conventional poly(acrylamide)/poly(acrylate) copolymers undergo syneresis and shrink, the gels formed by hydrophobically-modified polymers in otherwise identical formulations undergo syneresis at approximately half the rate of the hydrophilic polymers. It is also observed that the cross-linking of the hydrophobically-modified poly(acrylamide) is less sensitive to the concentration of divalent ions (Ca^{2+} , Mg^{2+}).

The structure of another hydrophobically-modified poly(acrylamide) where the hydrophobic modification takes the

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form of replacing about 1 mole percent ($M/(M+N)=0.01$) of the acrylamide units with the hydrophobic monomer N-decylacrylamide is:



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This polymer can also be cross-linked using metal ions (Cr(III), Zr(IV)) and organic molecules (hexanal).

- 10 An additional feature of hydrophobically-modified polymers such as (d) and (e) is that they can be prevented from cross-linking in contact with hydrocarbon. The prevention of cross-linking can arise from two possible mechanisms. Firstly, the larger organic cross-linker can be removed from the polymer solution by
- 15 solubilisation in the contacting hydrocarbon. The cross-linker hexanal, which is solubilized by the hydrophobically-modified polyacrylamide, is readily soluble in hydrocarbon and can be extracted from the polymer solution. Secondly, the solution of hydrophobically-modified polymer can partly solubilize the
- 20 hydrocarbon which itself can be sufficient to prevent cross-linking. Thus a solution of hydrophobically-modified poly(acrylamide) with the metal ion cross-linker such as Cr(III) or a small water-soluble cross-linker such as formaldehyde can be prevented from cross-linking when mixed with hydrocarbon.

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CLAIMS

1. A compound for selectively blocking water bearing
subterranean formations, said compound being a
5 hydrophobically modified water soluble polymer capable of
being chemically cross-linked so as to produce a stable gel
for blocking a water-bearing formation from a hydrocarbon-
producing well, wherein said polymer is essentially linear,
thus defining a polymeric backbone, and hydrophobic groups
10 are located at random positions along the backbone.
2. The compound of claim 1, comprising 0.5 to 5 mole per cent of
a hydrophobic monomer.
- 15 3. The compound of claim 1, comprising functional groups capable
of being chemically cross-linked, said groups being part of a
hydrophilic section of the polymer.
4. The compound of claim 1, comprising functional groups capable
20 of being chemically cross-linked, said groups being part of a
hydrophobic section of the polymer.
5. The compound of claim 1, having a molecular weight of 50,000
or more.
25
6. A composition for selectively blocking water bearing
formations from a hydrocarbon producing well comprising a
compound in accordance with claim 1 and a chemical cross-
linking agent.
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7. The composition of claim 6, wherein the chemical cross-
linking agent is organic.

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8. The composition of claim 6, wherein the chemical cross-linking agent is an aldehyde or aldehyde derivative comprising at least 5 carbon atoms.
- 5 9. The composition of claim 6, wherein the chemical cross-linking agent is hexanal or heptanal.

INTERNATIONAL SEARCH REPORT

Inter. Appl. No.

PCT/GB 99/00737

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 E21B43/02 C09K7/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 E21B C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 702 319 A (BOCK JAN ET AL) 27 October 1987 see claims 1-10; examples 1-18,44	1-5
Y		6-8
A	see the whole document ---	9
X	US 4 814 096 A (EVANI SYAMALARAO) 21 March 1989 see claims 1-14; examples 1-10	1-5
Y		6-8
A	see the whole document ---	9
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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X	US 4 856 588 A (BORCHARDT JOHN K) 15 August 1989 see column 4, line 16 - line 33 see column 5, line 1 - line 23; claims 1-22; examples 1-6	1-5
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